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(54) Title of the Invention:

MULLITE-CONTAINING MATERIAL, ITS PRODUCTION AND USE

(57) Abstract:

Mullite-containing material from a colloidal sol-gel process, whose precursors, in the form of aqueous dispersions with a solids content of 10-85 wt.%, are finely dispersed, pyrogenic metal oxide particles that contain silicon and aluminum or finely dispersed, pyrogenic metal

oxide particles that contain silicon and/or aluminum and a substance or substances that are dissolved in the dispersion and contain silicon and/or aluminum, and are subjected to a heat treatment at 1,000-1,700°C to obtain a material with a mullite content of at least 60%. In addition, the production of the mullite-containing material and its use for coating surfaces and for producing molded articles are described.

SPECIFICATION

[0001] The object of the invention is a mullite-containing material produced by a colloidal sol-gel process with the use of pyrogenic precursors, its production and use.

[0002] Mullite is an aluminum-silicon mixed oxide with a composition between $2Al_2O_3 \bullet SiO_2$ and $3Al_2O_3 \bullet 2SiO_2$. Mullite is known for its creep strength, high-temperature stability, chemical resistance, and low thermal expansion.

[0003] These properties make mullite an important material for coating the surfaces of heavily stressed materials. Especially in the case of composite materials, it is important, for example, to prevent the oxidation of reinforcing materials.

[0004] Mullite is synthesized basically by a powder route, a sol-gel route or by deposition methods via vapor phases.

[0005] To achieve complete mullitization by the powder route, starting from aluminum oxide and silicon dioxide, it is necessary to use sintering temperatures of more than 1,650°C, and this is accompanied by large volume contractions of up to 20% (which can lead to cracks).

[0006] Additives can be used to lower this temperature, but the disadvantage here is that these additives usually remain in the material and may have adverse effects on the properties of the mullite.

[0007] In the sol-gel route, which is based on hydrolysis and polycondensation reactions of precursor compounds in dissolved form, a sol is formed and then a gel, which is subsequently treated at elevated temperatures.

[0008] A disadvantage here is the low density of the gel body, which can shrink a great deal during the drying and sintering process. This can lead, for example, to the formation of bubbles and cracks in the coating.

[0009] Finally, there are techniques based on the deposition of mullite via the vapor phase, such as CVD (chemical vapor deposition) and PVD (physical vapor deposition). These methods are very time-consuming and expensive.

[0010] Therefore, the objective of the invention is to prepare a mullite-containing material that avoids the aforementioned disadvantages of the prior art, especially high sintering temperatures and cracking, and can be economically produced.

[0011] This objective is achieved by producing the mullite-containing material by a colloidal sol-gel process, whose precursors, in the form of aqueous dispersions with a solids content of 10-85 wt.%, are finely dispersed, pyrogenic metal oxide particles that contain silicon and aluminum or finely dispersed, pyrogenic metal oxide particles that contain silicon and/or aluminum and a substance or substances that are dissolved in the dispersion and contain silicon and/or aluminum, and are subjected to a heat treatment at 1,000-1,700°C to obtain a material with a mullite content of at least 60%.

[0012] In accordance with a special embodiment, the temperature of the heat treatment is 1,150-1,300°C.

[0013] The mullite-containing material of the invention preferably has a density of 80% or more of the theoretical density of mullite.

[0014] A mullite-containing material is understood to mean an aluminum-silicon mixed oxide with an aluminum oxide content of 71.8 to 77.2 wt.%. In addition, the material can contain up to 40% of aluminum oxide and/or silicon dioxide and/or other aluminum-silicon mixed oxides. The term colloidal sol-gel process refers in this connection to the presence of pyrogenic particles that are already precompressed. Pyrogenic particles are particles that can be obtained by well-known methods, especially flame hydrolysis, at high temperatures from the gas phase.

[0015] An essential aspect of the invention is the use of finely dispersed, pyrogenic metal oxide particles that are already precompressed during their production process and have no pores or only a small number of pores. With these particles, it is possible to produce highly filled dispersions, which require a low sintering temperature to produce mullitization and have a high density with little or no tendency to crack.

[0016] The finely dispersed, pyrogenic metal oxide particles on which the mullite-containing material of the invention is based may comprise silicon dioxide and/or aluminum dioxide and/or silicon-aluminum mixed oxide and/or mixtures thereof. Silicon dioxide particles of this type are described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A23, pp. 635 ff. Pyrogenically produced aluminum oxide is described, for example, in EP 1 083 151 A. The production of pyrogenic silicon-aluminum mixed oxide is described, for example, in EP 1 048 617 A or EP 995 718 A.

[0017] Pyrogenic silicon dioxide and pyrogenic aluminum oxide are especially advantageous as precursor compounds for the mullite-containing material.

[0018] The pyrogenic particles for producing the mullite-containing material of the invention preferably have a BET specific surface, determined by DIN 66131, of 10-400 m^2/g.

[0019] In accordance with a special embodiment, the precursor compounds of the mullite-containing material of the invention can also consist of pyrogenic particles that have been compressed to granules with a compacted density of 150-800 g/L. One possible method of producing granules of this type is described in DE 196 01 415 A for the example of silicon dioxide.

[0020] The substances dissolved in the dispersion can comprise salts of aluminum and/or silicon, organometallic compounds of aluminum and/or silicon, and mixtures thereof.

[0021] It is especially advantageous if the substances dissolved in the dispersion are tetraalkoxysilanes and/or their oligomers, and the pyrogenic metal oxide particles are aluminum oxide.

[0022] It is also especially advantageous if the substances dissolved in the dispersion are aluminum alcoholates, and the pyrogenic metal oxide particles are silicon dioxide.

[0023] The pH of the dispersion from which the mullite-containing material of the invention is produced can be adjusted with organic and/or inorganic acids or with organic and/or inorganic bases.

[0024] Examples of suitable organic acids are carboxylic acids of general formula $C_nH_{2n+1}CO_2H$, where preferably n = 0 to 6, dicarboxylic acids of general formula $HO_2C(CH_2)_nCO_2H$, where preferably n = 0 to 4, hydroxycarboxylic acids of general formula $RCH(OH)CO_2H$, where R = CH_3 or CH_2CO_2H or $CH(OH)CO_2H$, glycolic acid, pyruvic acid, salicylic acid or mixtures of these acids. Inorganic acids may be nitric acid, sulfuric acid or phosphoric acid.

[0025] Organic bases may be triethylamine, pyridine or tetramethylammonium hydroxide or mixtures of these bases. Inorganic bases may be ammonia, potassium hydroxide,

calcium hydroxide, ammonium hydroxide or aluminum hydroxide or mixtures of these bases.

[0026] The aqueous dispersion may also contain additives in the form of polymeric compounds, ionic compounds and/or metal alkoxides to control the gelation and/or to increase the green strength. For example, metal alkoxides of formula $Me(OR)_x$, where Me stands for a metal, preferably silicon, R stands for an alkyl group, and x corresponds to the valence of the metal ion.

[0027] An additional object of the invention is a method for producing the mullite-containing material of the invention. An aqueous dispersion that contains pyrogenic silicon dioxide and pyrogenic aluminum oxide or that contains pyrogenic silicon-aluminum mixed oxide or mixtures of the above, in which the molar ratio of Al_2O_3/SiO_2 ranges from 50:50 to 80:20, is gelled, possibly purified and then sintered.

[0028] In accordance with a special embodiment, instead of using an aqueous dispersion, the method can also be carried out by using a mixture of dispersions that contain silicon dioxide and aluminum oxide, or silicon dioxide and silicon-aluminum mixed oxide, or aluminum oxide and silicon-aluminum mixed oxide.

[0029] Another method for producing the mullite-containing material is characterized by the fact that one uses an aqueous dispersion that contains pyrogenic silicon dioxide or pyrogenic aluminum oxide or pyrogenic silicon-aluminum mixed oxide or mixtures thereof and salts of aluminum and/or silicon, organometallic compounds of aluminum and/or silicon and mixtures thereof, in which the molar ratio of Al_2O_3/SiO_2 ranges from 50:50 to 80:20, and the aqueous dispersion is gelled, possibly purified and then sintered.

[0030] In both methods, the pH of the aqueous dispersion can be adjusted with organic and/or inorganic acids or with organic and/or inorganic bases.

[0031] Examples of suitable organic acids are carboxylic acids of general formula $C_nH_{2n+1}CO_2H$, where preferably n = 0 to 6, dicarboxylic acids of general formula $HO_2C(CH_2)_nCO_2H$, where preferably n = 0 to 4, hydroxycarboxylic acids of general formula $RCH(OH)CO_2H$, where R = CH_3 or CH_2CO_2H or $CH(OH)CO_2H$, glycolic acid, pyruvic acid, salicylic acid, or mixtures of these acids. Inorganic acids may be nitric acid, sulfuric acid, or phosphoric acid.

[0032] Organic bases may be triethylamine, pyridine, or tetramethylammonium hydroxide, or mixtures of these bases. Inorganic bases may be ammonia, potassium hydroxide, calcium hydroxide, ammonium hydroxide, or aluminum hydroxide, or mixtures of these bases.

[0033] In both methods, the aqueous dispersion may also contain additives in the form of polymeric compounds, ionic compounds, and/or metal alkoxides to control the gelation and/or to increase the green strength. For example, metal alkoxides of formula $Me(OR)_x$, where Me stands for a metal, preferably silicon, R stands for an alkyl group, and x corresponds to the valence of the metal ion.

[0034] The sintering temperature is preferably 1,000-1,700°C. Temperatures in the range of 1,150-1,300°C are especially preferred.

[0035] A further object of the invention is the use of the mullite-containing material of the invention for coating surfaces. In particular, surfaces that contain carbon materials and/or carbon-silicon materials can be coated. The mullite-containing material of the invention protects surfaces of these kinds, preferably at high temperatures, from oxidation, gas penetration, and mechanical effects, and lends mechanical stability to the material.

[0036] Furthermore, the mullite-containing material of the invention can be used to produce molded articles in machine manufacturing, apparatus manufacturing, and engine

manufacturing, in measuring technology, and in optical components. Due to the high solids density in the dispersion during the production of the mullite-containing material and the resulting low shrinkage during sintering, nonshrinking second phases can be introduced in the form of particles, fibers, flakes, etc. The mullite-containing material of the invention is an ideal matrix for reinforcing and/or wear-reducing phases. The moderate sintering temperatures facilitate the incorporation of carbon-containing phases.

Example 1

[0037] 75.42 g of pyrogenic aluminum oxide (aluminum oxide C, Degussa) and 30.62 g of pyrogenic silicon dioxide (Aerosil OX 50, Degussa) are introduced into 245 g of redistilled water with the use of a dissolver disk and predispersed at 2,000 rpm for 10 minutes. Dispersion is then carried out with an Ultra-Turrax at a shearing speed of 6,000 rpm for 15 minutes.

[0038] This dispersion is placed in a petri dish and gels in less than an hour. The gel is dried for 3 hours at 60°C. The dried gel is then heated in a standard atmosphere to 1,300°C at a heating rate of 5 K/min and maintained at this temperature for another 3 hours. The oven is then allowed to cool down without regulation.

[0039] In the phase analysis by x-ray diffraction analysis, the mullite is demonstrated as a single crystalline phase.

Example 2

[0040] 340 g of an aqueous 30 wt.% aluminum oxide dispersion (W 630, Degussa) and 132 g of an aqueous silicon dioxide dispersion (K 330, Degussa) are combined. The mixture gels within one hour. The gel is dried for 3 hours at 60°C. The dried gel is then heated in a

standard atmosphere to 1,300°C at a heating rate of 5 K/min and maintained at this temperature for another 3 hours. The oven is then allowed to cool down without regulation.

[0041] In the phase analysis by x-ray diffraction analysis, the mullite and γ-aluminum oxide are demonstrated as crystalline phases.

CLAIMS

1. Mullite-containing material from a colloidal sol-gel process, characterized by the fact that its precursors, in the form of aqueous dispersions with a solids content of 10-85 wt.%, are finely dispersed, pyrogenic metal oxide particles that contain silicon and aluminum or finely dispersed, pyrogenic metal oxide particles that contain silicon and/or aluminum and a substance or substances that are dissolved in the dispersion and contain silicon and/or aluminum, and are subjected to a heat treatment at 1,000-1,700°C to obtain a material with a mullite content of at least 60%.

2. Mullite-containing material in accordance with Claim 1, characterized by the fact that the temperature of the heat treatment is 1,150-1,300°C.

3. Mullite-containing material in accordance with Claim 1 or Claim 2, characterized by the fact that it has a density of 80% or more of the theoretical density of mullite.

4. Mullite-containing material in accordance with Claims 1 to 3, characterized by the fact that the finely dispersed, pyrogenic metal oxide particles comprise silicon dioxide and/or aluminum oxide and/or silicon-aluminum mixed oxide and/or mixtures thereof.

5. Mullite-containing material in accordance with Claims 1 to 4, characterized by the fact that the pyrogenic metal oxide particles are aluminum oxide and silicon dioxide.

6. Mullite-containing material in accordance with Claims 1 to 5, characterized by the fact that the finely dispersed, pyrogenic metal oxide particles have a BET specific surface of 10-400 m^2/g.

7. Mullite-containing material in accordance with Claims 1 to 6, characterized by the fact that the pyrogenic metal oxide particles are compressed to granules with a tamped density of 150-800 g/L.

8. Mullite-containing material in accordance with Claims 1 to 7, characterized by the fact that the substances dissolved in the aqueous dispersion comprise salts of aluminum and/or silicon, organometallic compounds or aluminum and/or silicon and mixtures thereof.

9. Mullite-containing material in accordance with Claims 1 to 8, characterized by the fact that the pyrogenic metal oxide particles are aluminum oxide, and the substances dissolved in the aqueous dispersion are tetraalkoxysilanes and/or their oligomers.

10. Mullite-containing material in accordance with Claims 1 to 8, characterized by the fact that the pyrogenic metal oxide particles are silicon dioxide, and the substances dissolved in the dispersion are aluminum alcoholates.

11. Mullite-containing material in accordance with Claims 1 to 10, characterized by the fact that the pH of the aqueous dispersion is adjusted with organic and/or inorganic acids or with organic and/or inorganic bases.

12. Mullite-containing material in accordance with Claims 1 to 11, characterized by the fact that the aqueous dispersion contains polymeric compounds, ionic compounds and/or metal alkoxides as additives to control the gelation and/or to increase the green strength.

13. Method for producing the mullite-containing material in accordance with Claims 1 to 12, characterized by the fact that an aqueous dispersion that contains pyrogenic silicon dioxide and pyrogenic aluminum oxide or that contains pyrogenic silicon-aluminum mixed oxide or mixtures of the above, in which the molar ratio of Al_2O_3/SiO_2 ranges from 50:50 to 80:20, is gelled, possibly purified and then sintered.

14. Method in accordance with Claim 13, characterized by the fact that the aqueous dispersion is a mixture of dispersions that contain silicon dioxide and aluminum oxide, or silicon dioxide and silicon-aluminum mixed oxide, or aluminum oxide and silicon-aluminum mixed

oxide.

15. Method for producing the mullite-containing material in accordance with Claims 1 to 12, characterized by the fact that an aqueous dispersion that contains pyrogenic silicon dioxide or pyrogenic aluminum oxide or pyrogenic silicon-aluminum mixed oxide or mixtures thereof and salts of aluminum and/or silicon, organometallic compounds of aluminum and/or silicon and mixtures thereof, in which the molar ratio of Al_2O_3/SiO_2 ranges from 50:50 to 80:20, is gelled, possibly purified, and then sintered.

16. Method in accordance with Claims 13 to 15, characterized by the fact that the pH of the aqueous dispersion is adjusted with organic and/or inorganic acids or with organic and/or inorganic bases.

17. Method in accordance with Claims 13 to 16, characterized by the fact that polymeric and/or ionic compounds are added to the aqueous dispersion as additives to control the gelation and/or to increase the green strength.

18. Method in accordance with Claims 13 to 17, characterized by the fact that the sintering temperature is 1,000-1,700°C, and preferably 1,150-1,300°C.

19. Use of the mullite-containing material in accordance with Claims 1 to 12 for coating surfaces.

20. Use of the mullite-containing material in accordance with Claims 1 to 12 for producing molded articles in machine manufacturing, apparatus manufacturing, and engine manufacturing, in measuring technology, and in optical components.

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EUROPEAN SEARCH REPORT

Application No.:
EP 01 11 4055

RELEVANT DOCUMENTS

Category	Characterization of the Document with Indication, if Necessary, of the Relevant Parts	Pertains to Claim	Classification of the Application (Intl. Cl.7):
X	US 5,380,687 A (KLEINSCHMIT, PETER ET AL.) January 10, 1995 * Column 1, Line 28 to Column 2, Line 26; Example 1 * ---	1-7, 13	C04B14/04
A	DD 294 930 A (WETRO FEUERFESTWERKE) October 17, 1991 Page 2, last paragraph ---	1, 13	
X	US 5,064,783 A (LUCKEVICH, LYDIA M.) November 12, 1991) * Column 1, Line 5 to Line 12 * * Column 3, Line 64 to Column 4, Line 2 *	1, 12, 13, 15	Areas Searched (Intl. Cl.7): C04B

The present search report was prepared for all patent claims.

Search Location	Completion Date of the Search	Examiner
MUNICH	December 19, 2001	Rauscher, M.

CATEGORY OF THE CITED DOCUMENTS

X: of special importance considered alone
Y: of special importance in association with another publication of the same category
A: technological background
O: unwritten disclosure
P: interim literature

T: theories or principles on which the the invention is based
E: older patent document, but published on or after the application date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, agreeing document

APPENDIX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 11 4055

This Appendix lists the members of the patent families of the patent documents cited in the above-cited European Search Report.

The information on the family members reflects the current status of the database of the European Patent Office as of:

December 19, 2001.

This information is provided for assistance only; no liability is assumed.

Patent Document Cited in the Search Report	Date of Publication	Member(s) of the Patent Family	Date of Publication
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		EP 0,585,544 A1	March 9, 1994
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US 5,064,783 A	November 12, 1991	NONE	

For more details on this Appendix, see the Bulletin of the European Patent Office, No. 12/82.